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RESEARCH IN ELECTRON EMISSION FROM SEMICONDUCTORS

Report No. 19 Contract DA36-039 AMC-02221(E) 3rd Quarterly Report (Continuation of Contracts DA36-039 SC-87388 and DA36-039 SC-78155)

Department of the Army Subtask No.: 1G6-22001-A-055-01-07

Period Covered: 1 November 1963 to 31 January 1964

Objective: Research leading to a better theoretical understanding of

thermionic and hot electron emission and to new materials

with useful electron emission characteristics.

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A. Morton, Director Conversion Devices Laboratory

RADIO CORPORATION OF AMERICA Electronic Components and Devices Conversion Devices Laboratory RCA Laboratories Princeton, N. J.

February 11, 1964

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PURPOSE

Electron emission is to be studied with emphasis on the following aspects:

- (1) Basic investigation of hot electron emission, with the voltage applied across a semiconductor p-n junction varying over a wide range.
- (2) Production of low electron affinity surfaces by suitable activation processes with alkali metals.
- (3) Development and study of large area p-n junction hot electron emitters with injecting contacts.
- (4) Investigation of negative electron affinity materials for electron emission.

ABSTRACT

Experiments directed toward producing a clean surface on silicon by means of vacuum etching using HF molecules directed at silicon with oxide surfaces are reported. Results indicate that this treatment, along with moderate heat treatment, can produce increased hot electron emission.

A new method of mounting silicon hot electron emitters is described which is designed to minimize breakage of these fragile devices. Preliminary measurements of spectral distribution of light emitted from reverse biased silicon p-n junctions are reported.

Evidence for a negative electron affinity in GaP based on measurements of the spectral response of photoemission and the kinetic energy distribution of photoemitted electrons from heavily zinc doped GaP treated with cesium is reported.

CONFERENCES

During the last quarter, the following conference took place for the purpose of discussing work in progress under the contract:

Place: RCA Laboratories, Princeton, N.J.

Date: November 27, 1963

Attendance: Signal Corps - Dr. D. Dobischek and Mr. L. Kaplan

RCA - Messrs. Morton, Simon, Gatchell and Fuselier

FACTUAL DATA

I. Hot Electron Emission

A. Introduction

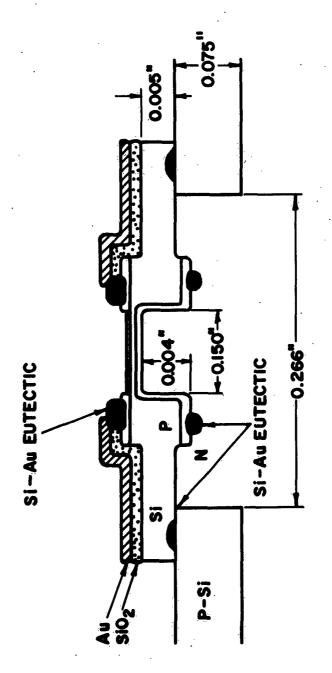
Two principal problems which continue to limit our ability to measure hot electron emission from silicon with a reverse biased vacuum emitter junction and an injecting contact were attacked during this quarter. A solution to the problem of mounting these devices so that they can be handled without breakage was sought. Attempts to solve the problem of cleaning the surface of electron emitters prior to cesium treatment were made using an HF vacuum etching technique.

In addition, measurements on the spectral response of light emission from reverse biased p-n junctions have been continued in order to obtain information on the energy distribution of the hot electrons in silicon.

B. Injecting Contact Fabrication

There has always been difficulty in holding and mounting the injecting contact devices. In fact, more than half our devices have been lost due to breakage in mounting. One of the major efforts during the past quarter was to solve the mounting problem.

The device, mounted as shown in Fig. 1, is fastened rigidly enough for any handling. Firstly, an SiO₂ layer is deposited on the emitter side by thermally decomposing orthoethylsilicate. The oxide is deposited after the appropriate number of boiling water-HF treatments which reduce the thickness of the emitter. The device is then alloyed, using a Au-Si preform, to a p-type silicon disk which is 0.75" in diameter, 0.075" thick, and has a 0.266" hole in the center. Hence, the thin, fragile silicon wafer on which the device is constructed is fastened to a rigid silicon disk which can be conveniently handled.



NEW MOUNT AND CONTACT CONFIGURATION

FIG. 1

This disk becomes the electrical contact to the base or p-region of the device. To make the contact to the emitter and injecting regions, Si-Au eutectic preforms are alloyed at the eutectic temperature. Si-Au eutectic preforms are used to prevent alloying through the contact regions which are slightly more than 2 microns deep. Lastly, Au is evaporated over the entire emitter side of the device. The emitter window is exposed by removing the gold using aqua regia. The gold is also removed around the edges to prevent shorting to the p-region. In this way, the gold covering the front (emitter) surface serves the dual purpose of providing an equipotential surface, which is desirable for velocity distribution measurements, and allows one to make electrical contact where the wafer is well supported. Note that the gold film is insulated from the p-region by the SiO₂ layer. This kind of construction is identical to that used in the fabrication of planar transistors. Contact to the injection region is easily made by either inserting a gold wire into the eutectic melt or by resting a probe against the eutectic.

C. Surface Treatment for Cleaning Si

In order to optimize hot electron emission from silicon, a clean surface is highly desirable for two reasons. First, any oxide layer presents unneeded material which the hot electrons must penetrate. Second, and more important, previous measurements have shown that the electron affinity for Cs on clean silicon is about 1.5 ev while the electron affinity for Cs on silicon with an oxide layer may be as high as 2.3 ev. Furthermore, previous experiments have shown that the first cesium monolayer appears to be tightly bound to clean silicon while it is not tightly bound to oxidized silicon. Since low electron affinity and stability are primary requirements for a hot electron emitter, it was decided to concentrate more effort on the surface problem.

The conventional methods of obtaining a clean silicon surface in a vacuum are heat treatment and argon bombardment. Both of these methods degrade the thin junction and are therefore of no use in conjunction with a hot electron emitter. A third method is chemical cleaning. Moll and his coworkers reported an increase in hot electron emission using a heated source of NH4HF to produce HF in vacuum to clean silicon. Our experience has been that this treatment left a white deposit on the crystal. It was believed that the introduction of pure HF gas in the system would be a cleaner procedure to use.

The first experiment was tried with HF gas on a heavily oxidized crystal. The thickness of the oxide was such that a red interference fringe could clearly be seen. A change in interference color would then indicate that the oxide was being removed. The HF was contained in a 3-inch section of copper tubing valved at either end with monel valves utilizing teflon gaskets. The experimental arrangement is shown in Fig. 2. The system was pumped and baked, and a pressure of $6x10^{-8}$ Torr was achieved. Valve A was opened with valve B shut, then valve A shut and valve B opened admitting a burst of HF gas directed at the crystal. No effect was observed with four successive bursts of HF gas. The crystal was then heated by passing a current through it which was increased with successive bursts. At a temperature of about 750°C, no change in interference color had been seen. The tube was then sealed off and allowed to stand overnight with HF in the system. The next morning, there were changes in the oxide coating interference color indicating that some of the oxide had been etched. Water vapor is liberated during the sealing-off operation so that this is consistent with the hypothesis, verified later in a chemistry reference, 2 that anhydrous HF does not etch SiO2.

^{1.} D.J. Bartelink, J.L. Moll and N.I. Meyer, Phys. Rev. 130, 972(1963).

^{2.} H. Remy, <u>Treatise on Inorganic Chemistry</u>, Elsevier Publishing Co., Amsterdam, Vol. 1, p. 790, 1956.

FIG. 2

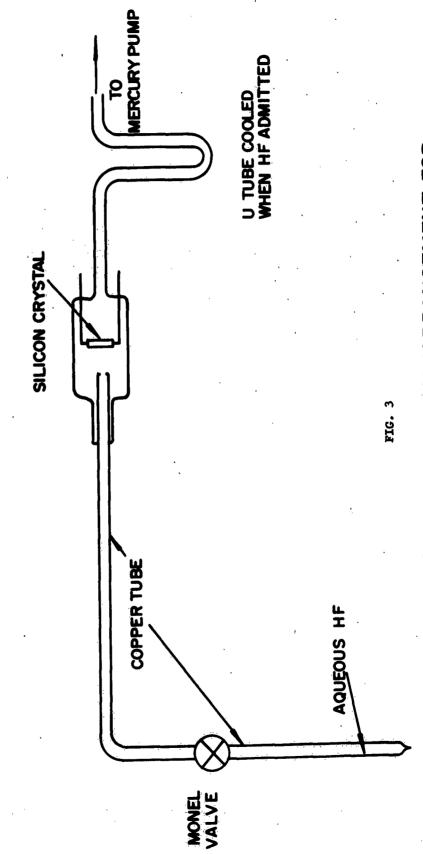
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The removal of enough SiO₂ to see interference color changes is a rather severe requirement to impose. Since the removal of only a thin oxide layer is necessary on a hot electron emitter, it was decided that an effect on hot electron emission would be a much more sensitive test. A grown junction, with the plane of the junction intersecting the surface was chosen for the next experiment. This system should provide a very sensitive test of oxide removal since the hot electrons have only an oxide to pass through and therefore removal of the oxide should enhance emission.

The crystal with the grown junction was mounted in a tube. The tube was pumped and baked, and a small hot electron emission current was detected. The crystal was then removed and mounted in a tube similar to the one shown in Fig. 3. Aqueous hydrofluoric acid was contained in the pinched-off copper tube below the valve. This section was cooled to 77° K, the valve opened, and the tube pumped. The valve was then shut and the system baked up the the valve. There appeared to be a slightly copper colored deposit on the walls of the tube. The temperature of the HF was raised from 77° K to 200° K and then to room temperature with the crystal at room temperature and the valve opened. During this period, a reverse bias was repeatedly applied to the junction in an attempt to detect hot electron emission. No hot electron emission greater than $3x10^{-14}$ amps could be detected.

The temperature of the crystal was gradually raised with the HF source at room temperature. After heat treatment with a current of 150 ma, an emission current of 5x10⁻¹⁴ amps was detected. Further heat treatment was given to the crystal in an attempt to maximize the emission. The effects of the heat treatment are summarized as follows.

DIRECTING HF MOLECULES AT SILICON IN VACUUM SECOND EXPERIMENTAL ARRANGEMENT FOR



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I.

Cryst	al Treatment	Bias Across Junction	Hot Electron Emission
	led-off bulb with	100	.2×10 ⁻¹³
11	11 11	105	.4×10 ⁻¹³
11	11 11 1	110	1.5×10 ⁻¹³
	150 ma heat treatmen sence of HF (T<550°C		.5×10 ⁻¹³
	neat treatment at	80	.8×10 ⁻¹³
	neat treatment at n presence of HF	60	

The last three voltages listed are the maximum voltages the crystal could tolerate without thermal runaway. It should be noted that progressive heat treatment lowered this voltage. Since hot electron emission increases very rapidly with voltage across the junction, it is difficult to draw meaningful conclusions from hot electron emission data at different bias voltages.

A new system has been designed which will contain independent sources for HF gas and water vapor so that the temperature and therefore vapor pressure of each constituent can be controlled independently. This will allow much lower rates of admission of H₂O and HF into the system than was possible in the present arrangement.

D. Light Emission from Hot Electron Emitters

In the First Quarterly Report, it was mentioned that spectral distribution measurements of the light emission coming from the reverse biased emitters would be of interest. The interest lies in the strong possibility of determining from the spectral distribution the electron energy distribution in the conduction band as a function of reverse bias on the emitter junction.

Apparatus has been constructed and assembled to measure the spectral distribution. A block diagram of the apparatus is given in Fig. 4.

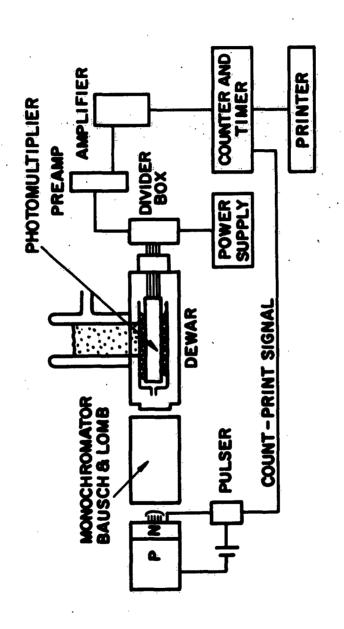
As a first experiment before attempting measurements on an injecting contact, it was decided to attempt to repeat Chynoweth's results³ on a p-n junction in order to check out the experimental setup. To this end, an emitter junction of an ordinary silicon transistor was used as a light source. When this device was placed before the monochromator, the detection system showed substantial signal-to-noise ratio indicating a spectrum measurement would be possible. A spectrum was measured in the range of 2.92 ev to 1.60 ev and is given in Fig. 5. The energy, 2.92 ev, is close to the high energy cut-off as reported by Chynoweth. The energy, 1.60 ev, is in the photothreshold tail of the photocathode of the RCA7265 photomultiplier tube used to measure this portion of the spectrum.

Fig. 5 consists of two curves. The ordinate scale represents photons per unit energy in arbitrary units. One curve is corrected for the photocathode response and one is not. It should be noted here that the photocathode response was measured at room temperature (300°K) whereas the measurements were taken with the photocathode at 77°K. This introduces a considerable error in the tail of the photoresponse and hence in the correction to be applied to the data.

Fig. 6 is a comparison of Chynoweth's and our results. It can be seen that comparison is fair for the high energy end. The poor comparison in the low energy is twofold: Firstly, as mentioned above, the photocathode response was measured at 300°K whereas the light emission measurements were made at 77°K. The correction to be applied would most certainly raise the low energy points.

^{3.} A.G. Chynoweth and K.G. McKay, Phys. Rev. 102, 369(1956).

^{4.} W.E. Spicer, J. Appl. Phys. 31, 2077(1960).



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EXPERIMENTAL ARRANGEMENT FOR MEASURING LIGHT EMISSION SPECTRAL RESPONSE

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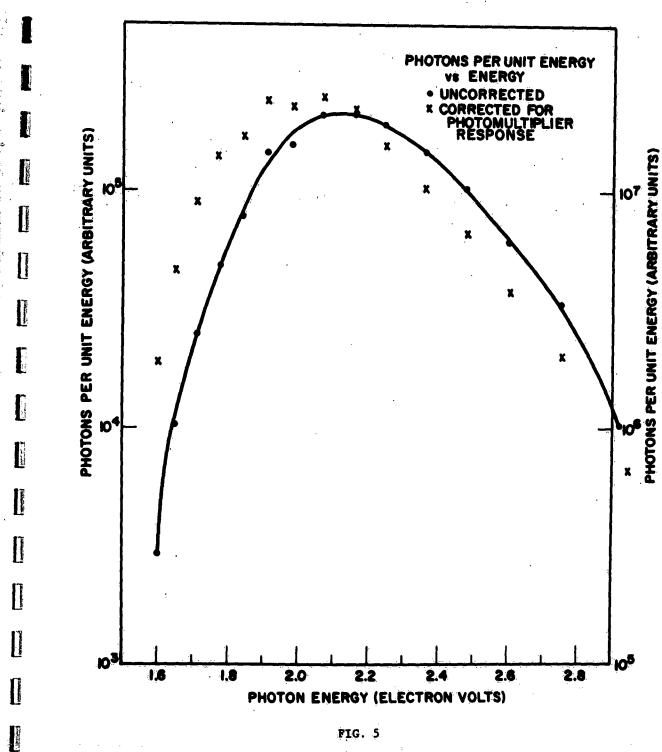
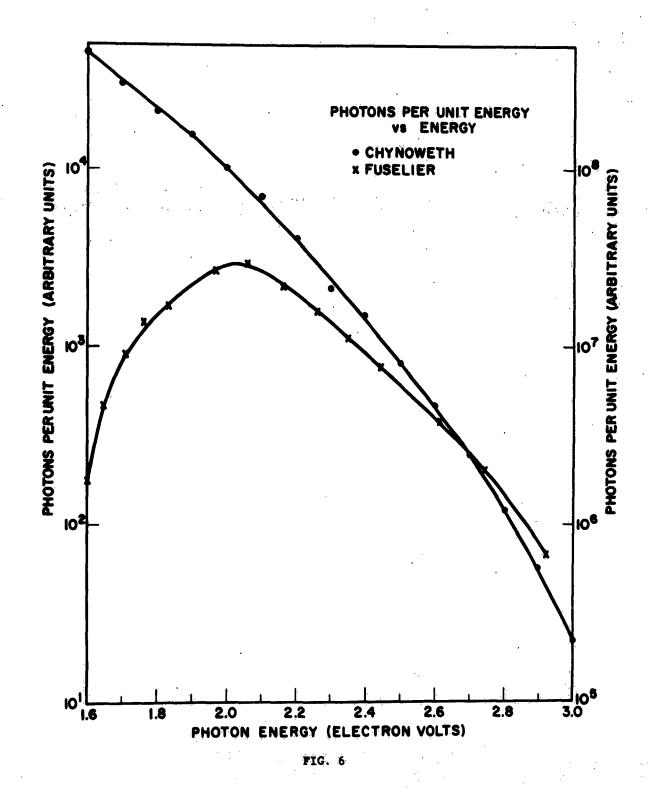


FIG. 5



This correction would extend up to 2.2 ev. Secondly, due to the alloyed contact region which covers most of the emitter, a large percentage of the light emitted comes from the junction edge making a correction for self absorption impossible. About all that can be said about absorption corrections is that in the high energy region most of the light will come from the edge since it is highly absorbed elsewhere. In the low energy range, the total light emitted will be divided between that from the edge and that generated below the surface. The inferred result is that the high energy points will be pushed up slightly.

It can be seen by looking at Fig. 6 that if the above mentioned corrections are applied, it is not unreasonable to expect our data to agree with that of Chynoweth.

In the next quarter, the spectral response of the light emission from an injecting contact will be measured. The spectral response of the photocathode will be measured at operating temperature. Also, there is no problem with edge emission since there is no junction edge on an injecting contact hot electron emitter.

II. Negative Electron Affinity Material

A. Introduction

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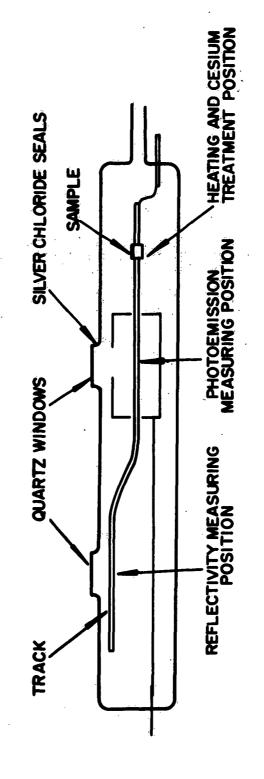
By depositing cesium on a wide band gap p-type semiconductor, it is possible to produce band bending such that the conduction band in the bulk material lies at an energy higher than the vacuum potential. In a material with a very high acceptor impurity concentration, the band bending should occur within an electron mean free path of the surface so that electrons injected into or excited in the conduction band in the bulk can be emitted into vacuum. Such a material might have desirable properties as an electron emitter; in particular, high efficiency and low velocity spread. This band bending effect can be demonstrated by means of photoemission measurements in which electrons are excited in the bulk into different conduction band energy states.

B. Experimental Measurements

During this quarter, our efforts have been directed toward demonstrating this effect in GaP heavily doped with zinc; as described in the previous quarterly report. The sample consists of a thin wafer cut from a large-grained polycrystalline ingot of GaP purchased from Merck and Co. The GaP was treated at 1200° C for two hours in zinc vapor to produce a sample with a resistivity of 1.1×10^{-4} ohm-cm or a calculated impurity concentration of 7.6×10^{20} cm⁻³, assuming a hole mobility of 75 cm²v⁻¹sec⁻¹. The sample was optically polished and etched in a solution consisting of:

60 m1 HNO₃
10 m1 HF
30 m1 H₂SO₄
10 drops Bromine

The sample was mounted on tracks in the tube shown in Fig. 7 so that it could be moved into several positions. In one position, the sample is close to and



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EXPERIMENTAL TUBE FOR MEASUREMENT OF REFLECTIVITY AND PHOTOEMISSION OF GAP

FIG. 7

in front of a quartz window to simplify reflectivity measurements. In the second position, the sample is in front of a quartz window in a cylindrical collector for photoemission measurements. In a third position, the crystal can be heated by conduction current and treated with cesium.

After evacuating the tube, the sample was heated to approximately 600°C for 1 hour. After cooling, the sample was treated with cesium until peak photoemission with white light was observed.

The sample reflectivity was measured after cesium treatment as well as before the sample was mounted in the tube as shown in Fig. 8. Also shown are measurements on an undoped sample which was optically polished and etched as was the doped sample. The measurements on the undoped sample are in excellent agreement with the highest reflectivities reported in the literature⁵ for GaP.

The doped sample has lower reflectivity apparently because the etching treatment tended to be much more sensitive to crystallite orientation than on the undoped sample. This resulted in a structure on the surface of some of the crystallites thus reducing their reflectivity. Fig. 9 is a photograph of the sample showing the crystal grain structure.

In order to investigate whether the crystallite structure affects the uniformity of the photoemission of the sample, photoemission was measured as the sample was scanned with a point light. The spot size on the sample was .010" in diameter. The spectral output of the source, a xenon crater arc lamp, is not known. However, the glass envelope restricts the spectral output to the visible and near ultraviolet. The sample was scanned along the positions shown by the horizontal reference lines on the inset in Fig. 10. The relative photoemissive sensitivity data as a function of position are shown

^{5.} H. Ehrenreich, H.R. Phillipp, J.C. Phillips, Phys. Rev. Ltrs. 8, 59(1962).

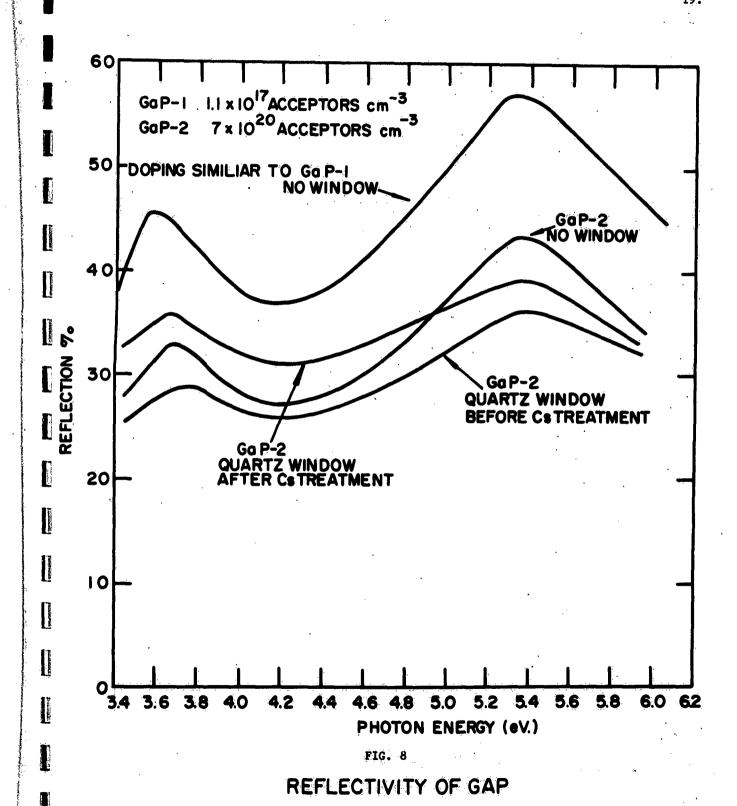
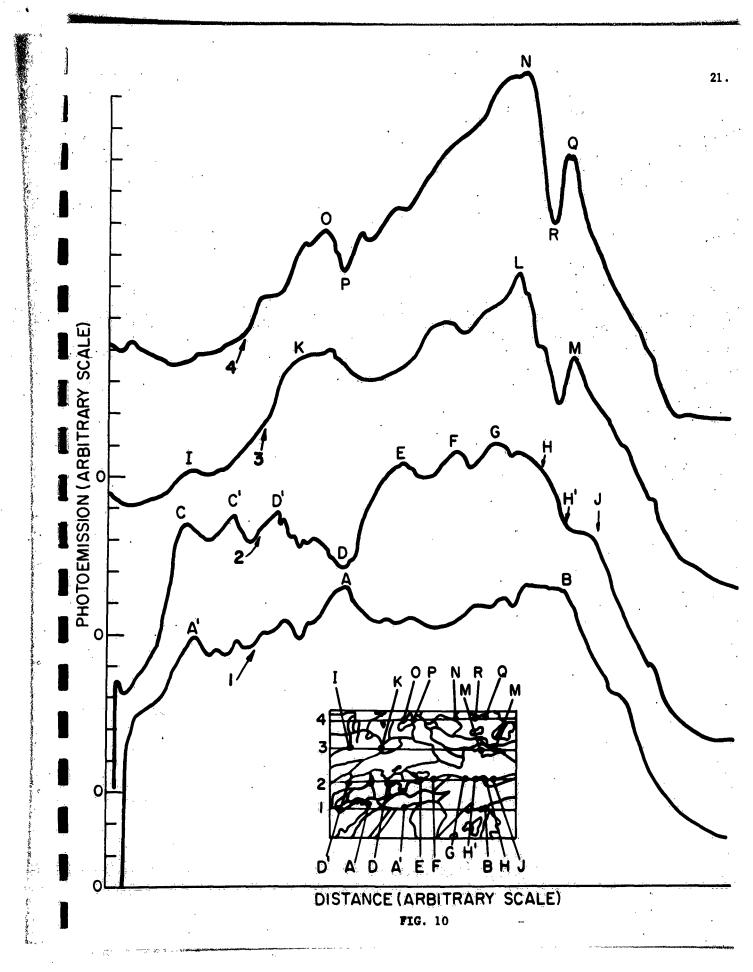




FIG. 9
Photograph of Grain Structure of GaP-2

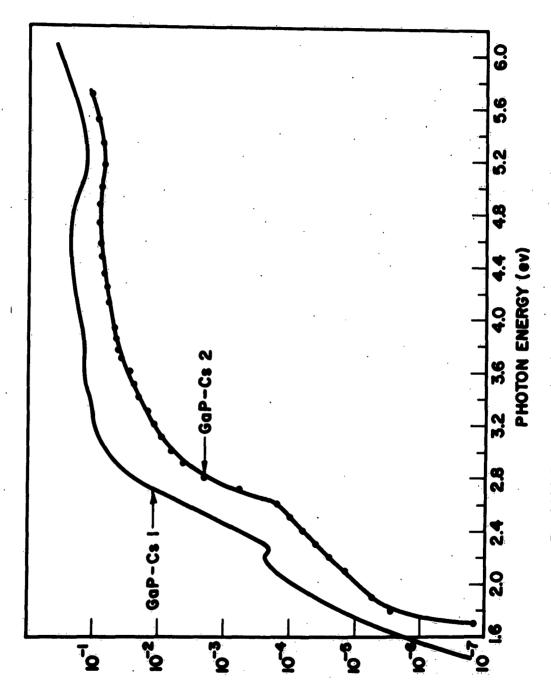


in Fig. 10. The structure in the photoemission as a function of position can be directly related to the polycrystalline structure of the sample as indicated on the inset in Fig. 10. The variation in sensitivity may be the result of variations in the cesium treatment or in the reflectivity of the surface. This effect can be eliminated, of course, with single crystal samples.

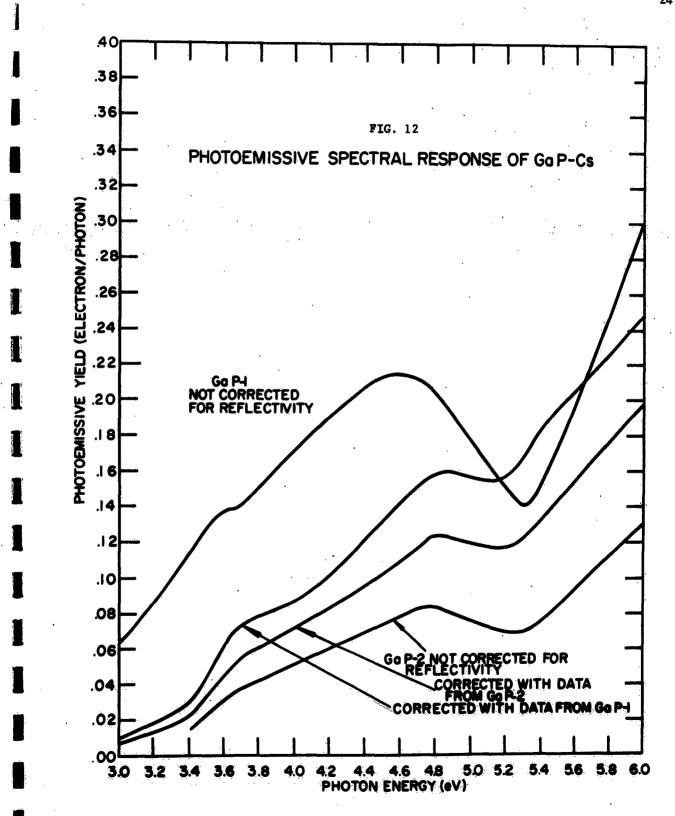
Measurements of the spectral response of the photoemissive yield are shown in Fig. 11 on a semi-logarithmic plot. Fig. 12 shows the spectral response plotted on a linear scale. Also shown are the data corrected for reflectivity using the reflectivity data taken on this sample and the highest reflectivities measured on an undoped sample. The spectral response measurements on GaP-1, a sample doped with 1.1x10¹⁷ cm⁻³ impurities, are also shown on Fig. 12.

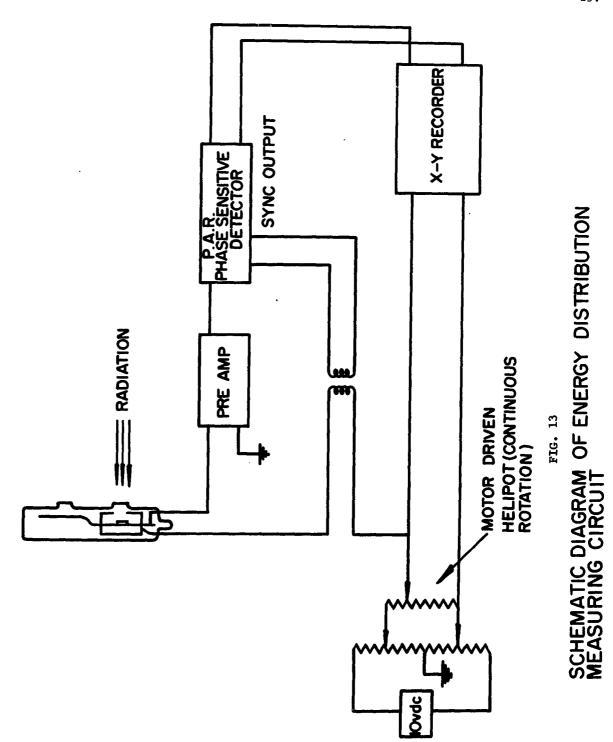
Measurements of the velocity distribution were made using a technique developed by Spicer. The experimental circuit is shown in Fig. 13. The method consists of applying a slowly varying retarding potential between the collector and the photocathode. Superimposed on this voltage is a small ac voltage (ΔV = .01 volts at 17 cps). The dc current in this circuit is proportional to the number of photoelectrons with energy greater than the retarding potential, V. The photoemissive ac current is proportional to the number of photoelectrons with energy in the range between V and V+ΔV, i.e., the ac photoemissive current is equal to the differentiated dc current. In addition to the photoemissive ac current, there is a capacitive ac current through the tube. Since this signal is out of phase with the photoemissive current, the phase-sensitive detector can be used to discriminate against it. The output of the phase-sensitive detector is a measure of the energy

^{6.} W.E. Spicer, J. Phys. Chem. Solids 22, 364(1961).



PHOTOEMISSIVE SPECTRAL RESPONSE OF GaP - Cs





distribution of the emitted electrons.

The energy distributions of the emitted electrons are shown in Fig. 14 with different photon energies incident on the sample. The measurements at photon energies below 5 ev were made using radiation from a Cary Model 14 Spectrophotometer which has a resolution of 35 A/mm. The data were normalized at the peak number of photoemitted electrons. Above 5 ev, the radiation from a Bausch and Lomb Monochromator with a resolution of 32 A/mm was used. In both cases, a slit width of 3 mm was used. The zero of kinetic energy of the emitted electrons cannot be obtained from measurement of the potential applied to the collector and the emitter because the contact potential between these elements is not known. The zero of kinetic energy can be obtained by extrapolating the distribution curves to zero energy as shown in Fig. 14. The small number of electrons observed with apparent kinetic energy below zero are probably due to inhomogeneities in the potential between the cathode and collector as a result of patch effect on the surfaces. The assignment of the zero kinetic energy can be checked from the relationship between the photothreshold \mathbf{E}_{th} , the maximum kinetic energy observed, and the incident photon energy:

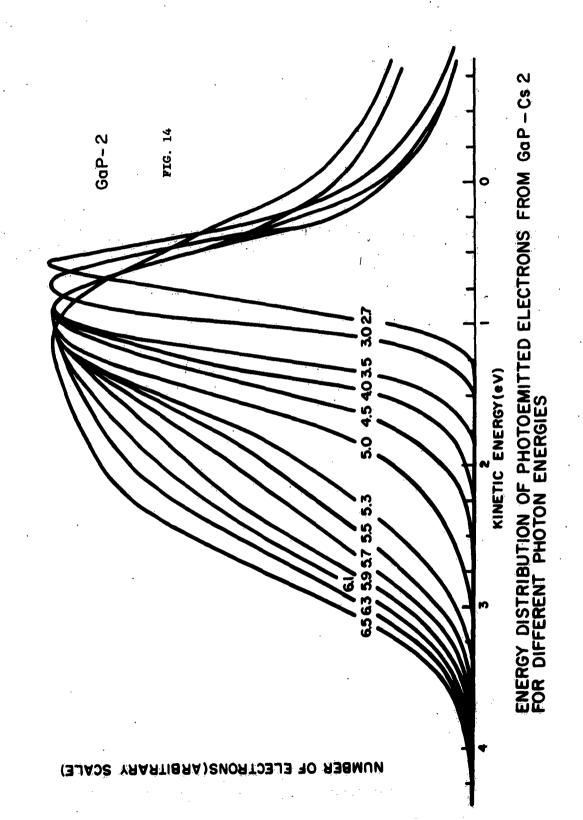
$$hv = E_{th} + (KE)_{max}$$
.

It is seen that this relationship is approximately satisfied at the photon energies used in these measurements.

C. Interpretation of Results

While no detailed calculations of the band structure of GaP have been published, Phillips has proposed the model of the band structure reproduced in Fig. 15 based on experimental measurements. The optical absorption structure is dominated by the transitions at 3.7 ev, 5.3 ev and 7 ev as shown

^{7.} J.C. Phillips, Phys. Rev. 133, A452(1964).



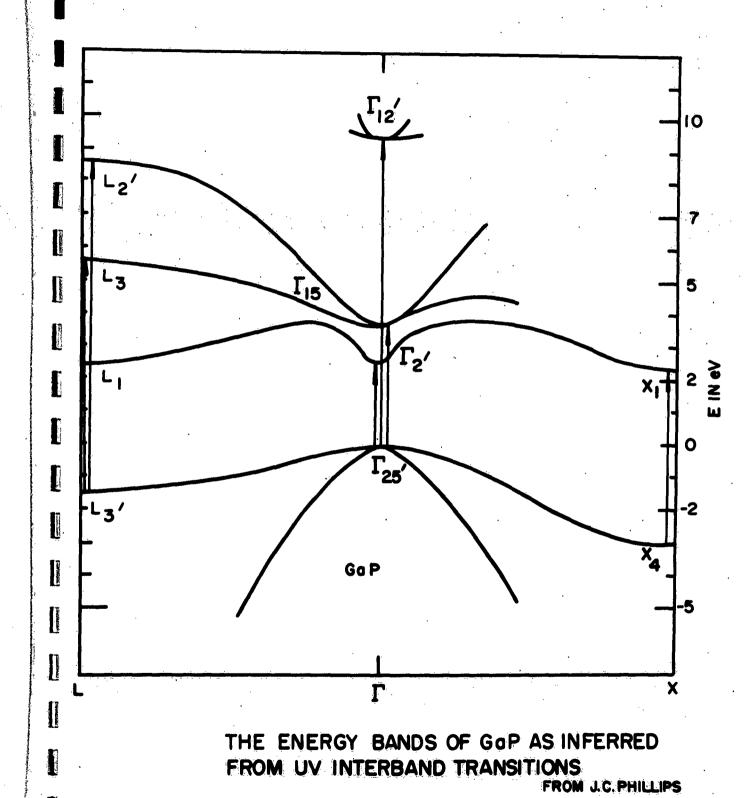


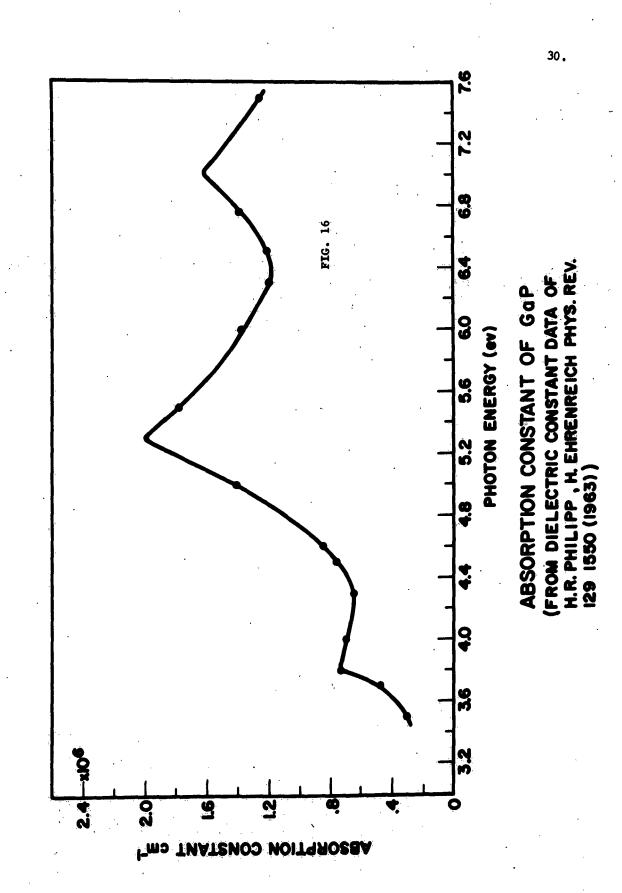
FIG. 15

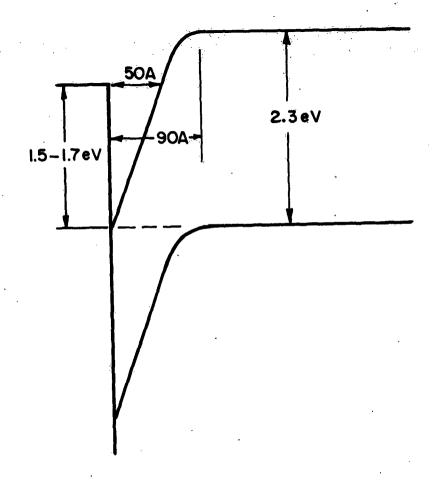
in Fig. 16. The absorption data were calculated from the published values of the real and imaginary parts of the dielectric constant. 8 In the 5.3 ev transition, an electron is excited from the valence band to the conduction band minimum. In the 3.7 ev transition, an electron is excited to a conduction band state 1.4 ev above the conduction band minimum while the final state in the 7 ev transition is at an energy of 3.3 ev above the conduction band minimum.

The band bending in GaP doped degenerately p-type is shown in Fig. 17. The values of the parameters have been estimated in the previous report. It should be noted that this estimate is based on a theoretical treatment valid only for non-degenerate material and the band bending is probably sharper than estimated.

The value of the electron affinity, 1.7 ev, is obtained from the threshold for photoemission. It is seen in Fig. 12 that, following the optical absorption, a peak occurs at 3.7 ev but that a slight minimum occurs at 5.3 ev. The minimum at 5.3 ev may be the result of the high absorption constant at this energy causing appreciable absorption in the region where the band bending occurs. The dip occurs because the electrons excited in that portion of the material where the conduction band is below the vacuum level cannot be emitted. The 3.7 ev transition and those transitions at energies above 5.3 ev occur to states above the vacuum level even in the bent band region so that the excited electrons can be emitted. The rapid increase in photoemission with energy above 5.3 ev is not understood. It seems that it must be explained in terms of the probability of escape of photoexcited electrons being a function of the electron energy in the conduction band. This conclusion is reached because while the absorption constant is decreasing, the photoemission is going

^{8.} H.R. Philipp and H. Ehrenreich, Phys. Rev. 129, 1550(1963).





Taura estate

BAND BENDING IN DEGENERATE
GOP WITH CESIUM ON SURFACE

up rapidly. The energies of the states with respect to the conduction band minimum into which the electrons are excited above 5.3 ev are going up, although rather slowly. It is this increase which it is hypothesized must give rise to an appreciable increase in escape depth from the sample. However, if the negative electron affinity effect is strong, the escape depth should be relatively independent of the energy to which electrons are excited since electrons which decay into the bottom of the conduction band should still be capable of being emitted.

Evidence in support of the negative electron affinity effect, on the other hand, can be found by comparing the spectral response of the heavily doped sample (GaP-2) with that of the less heavily doped sample (GaP-1). It can be seen that a considerable increase in the relative response at 5.3 ev is observed. This indicates that electrons excited into the conduction band minimum can indeed be emitted. It should be noted that the probable reason the yield of GaP-1 is larger than that of GaP-2 is that the electron affinity of GaP-1 is 1.4 ev while that of GaP-2 is 1.7 ev, apparently because of differences in the surface treatment.

The energy distribution of the emitted electrons shows a peak in the distribution at about 1 ev for electrons excited with photons varying from 3.5 ev to 6.5 ev although a second peak appears at a kinetic energy of approximately 2.3 ev. This result can be interpreted as being due to electrons excited at these energies decaying into the conduction band minimum and then drifting to the surface and being emitted, i.e., these results are consistent with the negative electron affinity effect. The other structure in the energy distribution curves could be the result of emission from the bent band region. These results imply that the negative electron affinity effect is present. One difficulty arises because it would be expected that this

peak would occur at .6 ev. This difficulty may disappear or be reduced when the emptying of the valence band due to the degenerate doping is taken into account.

Energy distribution measurements were made on GaP-1 also. However, apparently because of a severe contact potential difference across the collector, possibly the result of a non-uniform cesium deposition on the collector, the measurements are not valid.

To summarize the conclusions based on these measurements supporting the negative electron affinity model:

- (1) With increased doping, the relative emission in the 5.3 ev region (the bottom of the conduction band) is increased.
- (2) The energy distribution of the emitted electrons for most energies measured is similar, implying that most electrons come from the same energy level (the bottom of the conduction band.

Difficulties with the negative electron affinity model are:

- (1) The increasing photoemissive yield with photon energy above 5.3 ev is not explained.
- (2) The peak in the energy distribution of the emitted electrons is somewhat too small,

It should be noted that the interpretation of the data is based on a band structure model which has not been fully developed. Further measurements on samples with different dopings should yield information on the GaP band structure as well as the negative electron affinity effect.

III. Conclusions

- A method of mounting fragile silicon hot electron emitters with injecting contacts was developed.
- (2) Attempts to etch silicon dioxide in vacuum with anhydrous HF vapor indicated that HF does not etch SiO₂ appreciably when water vapor is not present.
- (3) A slight increase in hot electron emission was obtained from a silicon crystal with a p-n junction perpendicular to the surface when wet HF vapor was directed at the surface and the crystal was heated to relatively low temperature. This indicates that the surfaces of diffused silicon hot electron emitters can be cleaned with the HF vacuum treatment.
- (4) Preliminary measurements of the light emission from reverse biased p-n junctions indicate that the experimental apparatus is operating correctly.
- (5) Measurements of the photoemissive spectral response and the energy distribution of photoemitted electrons from heavily doped p-type GaP indicate that the negative electron affinity effect is present in this material. However, several difficulties with the interpretation remain to be resolved.

PROGRAM FOR NEXT QUARTER

- (1) Measure hot electron emission from silicon p-n junctions with an injecting contact which have been cleaned with HF and cesium treated.
- (2) Attempt to measure velocity distribution of electrons emitted from hot electron emitters.
- (3) Measure spectral distribution of light emitted from reverse biased p-n junctions with injecting contacts.
- (4) Measure photoemissive properties of GaP with several dopings in order to verify the existence of the negative electron affinity effect.

Man-hours expended for the period 1 November 1963 to 31 January 1964:

Administrative

G. A. Morton

23-1/4 hours

hours

95

Members of Technical Staff

C. R. Fuselier 389-1/2 hours E. K. Gatchell 342 hours R. E. Simon

Technicians

G. O. Fowler 39-3/4 hours D. F. Greene 129-1/4 hours C. D. Rowley 11-3/4 hours TOTAL MAN-HOURS 1030-1/2

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